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A GRAVIMETRIC TECHNIQUE FOR THE PREPARATION OF ACCURATE TRACE ORGANIC GAS STANDARDS

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A number of these gravimetric primary mixtures have been prepared and analytically intercompared using gas chromatography (GC) with flame-ionization detection (FID). Excellent agreement has been found between analyte concentration values prepared gravimetrically and concentration values determined by analysis.

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A GRAVIMETRIC TECHNIQUE FOR THE PREPARATION OF ACCURATE TRACE ORGANIC GAS STANDARDS

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Abstract

An accurate procedure based on micro-gravimetry has been used for the preparation of volatile, hazardous organic chemicals in a nitrogen matrix in pressurized gas cylinders at analyte concentrations ranging from 10 ppb to 10 ppm, by mole. In this technique, the organics of interest are individually weighed into separate glass capillary tubes using a micro-analytical balance. The tubes are sealed, and subsequently broken in a fixed line connected to an evacuated cylinder. A known weight of pre-analyzed matrix gas (nitrogen) is then used to pressurize the cylinder, and the concentrations of the organics are calculated on a molar basis relative to the number of moles of the matrix gas.

A number of these gravimetric primary mixtures have been prepared and analytically intercompared using gas chromatography (GC) with flame-ionization detection (FID). Excellent agreement has been found between analyte concentration values prepared gravimetrically and concentration values determined by analysis.

This paper will focus on a description of the micro-gravimetric technique and the analytical system, the estimation of specific uncer-tainties associated with the preparation of these mixtures, and how these uncertainties are used to assign a net uncertainty to the final analyte concentration. Particular attention is given to mixtures at the 10 to 150 ppb level. A brief description of how the overall network of gravimetric primary standards is used to provide long term, consistent data quality for trace organic gas mixtures is included.

Procedure

Liquid Organics

The organic analyte is introduced into an evacuated cylinder using a thin-walled glass capillary tube. One end of the capillary tube (ca. 1.6 mm o.d.) is drawn to a fine point, using a microburner. Another section of the capillary tubing is drawn out in a similar manner and broken off from the main part of the capillary tubing to obtain a sample tube (ca. 18 mm in length) having drawn out sections at each end. This represents a modification of the original procedure developed at NBS, in which a 100 mm by 1.6 mm o.d. capillary tube (drawn out at both ends) was used as the sample tube for preparing ppm and high ppb mixtures. One end of the sample tube is flame-sealed and weighed several times on an electronic microbalance to obtain an empty tube weight. A tare tube, sealed on both ends, is weighed immediately prior to and following the weighing of the sample tube to obtain a mean weight of the sample tube.

After obtaining an accurate weight of the empty sample tube, its open end is immersed in the organic liquid of interest in a test tube. A syringe is connected to the test tube with a short section of plastic tubing, and the syringe plunger is withdrawn to draw organic liquid up into the sample tube. The sample tube is then removed from the test tube and centrifuged to transfer the organic liquid to the sealed end of the capillary. The open end of the sample tube is then heat sealed.

Gaseous Organics

A modification to the above procedure is used for organics boiling below room temperature. In this modification, a test tube is placed in dry ice and the organic vapor is passed into the test tube where it liquifies. A weighed sample tube sealed at one end is then heated at the sealed end and its open end is placed into the test tube containing the liquified organic. The temperature gradient of the heated sample tube causes the liquid to be drawn up as the tube cools. The glass sample tube is then removed and placed in a cooled centrifuge tube, centrifuged, and its open end is heat-sealed.

For both liquid and gaseous organics, the fully sealed sample tubes containing the organic are weighed several times against a common tare to determine an accurate weight of the organic, making any correction necessary due to weight loss of the tube material from sealing the tube. Blank tubes, prepared in the same manner, are used to correct for weight loss due to sealing.

Preparation of Cylinder Mixtures

Aluminum gas cylinders equipped with Compressed Gas Association 350 valves used for the preparation of the mixtures were procured from commercial sources. The cylinders were evacuated, pressurized to about 3.5 MPa (500 psi) with nitrogen, heated slightly to desorb any trace organics from the walls and valve, and then re-evacuated. The cylinders were weighed on a top-loading balance against a tare cylinder. An appropriate stainless steel nut and nipple was placed on a given cylinder valve, and a short piece of teflon tubing was attached to the nipple by the use of stainless steel fittings. The internal diameter of the teflon tubing was such that a

sealed sample capillary tube containing the organic of interest could be snuggly fitted inside the teflon tubing. The sample tube was inserted so that the end containing the organic was furthest from the cylinder valve. The cylinder valve was opened slightly, and the empty end of the capillary was manually broken, *in situ*. A heat gun was used to slowly heat the capillary, vaporizing the organic into the evacuated cylinder. When all the organic appeared to be vaporized, the other end of the tube was crushed with pliers to allow room air to be pulled over the broken capillary to flush any residual organic into the cylinder. In the preparation of multi-component organic mixtures, care must be taken to ensure that sufficient vacuum is available to quantitatively load all the organics into the cylinders.

After all of the organics had been introduced into the cylinder along with an atmosphere of air, the cylinder was again weighed; the weight difference before and after loading the cylinder represented the weight of the added organics plus the weight of air. The cylinder was then pressurized with nitrogen (as the matrix gas) to approximately 12.4 MPa (1800 psi), and weighed a third time; the weight difference between the second and third weighings represented the weight of nitrogen added. The concentrations of the organics were calculated from the known number of moles of each of the added organics, relative to the total number of moles of nitrogen and air added to the cylinder.

Experimental

A group of six cylinder mixtures was prepared, each containing benzene, vinyl chloride, chloroform, carbon tetrachloride, and tetrachloroethylene in nitrogen, ranging in concentration from 3 to 150 ppb.

The reagents were obtained from appropriate commercial sources, analyzed using a GC equipped with an FID, and found to be 99.9+% pure, with no significant impurities. Analysis of the nitrogen matrix gas (GC-FID) was conducted to ascertain its purity and to ensure the absence of the organics employed for the preparation of the cylinder mixtures.

The GC-FID technique also was used to analyze and intercompare the organic gas mixtures, using a 6.1 m x 3.2 mm stainless steel column containing 10% SP 1000 on 100/120 inactivated support material. The analysis was performed isothermally at 80°C, with a nitrogen carrier flow rate of 30 mL/min. An automatic air-actuated sampling system equipped with a 10.0 cm^3 sampling loop was used to inject the sample onto the GC column.

Results and Discussion

To assess the accuracy of concentration values assigned to each organic in the six micrograviметrically-prepared standards, the individual uncertainties associated with the various steps in the preparation procedure must be identified and quantified. A discussion of this process follows.

Errors in Preparation

There are at least five principal sources of error in the preparation technique: (1) the uncertainty of purity of the organic reagents and the matrix gas; (2) the imprecision in determining the weight of empty and filled capillary sample tubes; (3) the uncertainty in the weight loss due to sealing; (4) the imprecision in the weight of the matrix gas; and (5) the possibility of a slight loss in organic in the *in situ* transfer from the sample tube to the evacuated cylinder.

The organic reagents were obtained at a specified purity of 99.9%. Analysis by GC-FID showed no detectable impurities in any of the organics analyzed. The uncertainty in the purity of each of the organics were therefore estimated not to exceed ±0.1% relative. The nitrogen matrix gas and room air were similarly analyzed for volatile impurities, as well as for traces of the organics used to prepare the cylinder mixtures (benzene, vinyl chloride, chloroform, carbon tetrachloride and tetrachloroethylene). No impurities due to traces of benzene or vinyl chloride were detected using a GC-FID system (limit of detection estimated to be 0.05 ppb). No impurities due to chloroform, carbon tetrachloride, or tetrachloroethylene were detected using a GC-ECD (electron capture detection) system (detectable limit estimated to be 1 ppt). The contamination uncertainties due to these detectable limits was estimated not to exceed ±1.5% relative for benzene and vinyl chloride, and ±0.03% relative for chloroform, carbon tetrachloride and tetrachloroethylene, at the 3 ppb level.

The imprecision in the weighing of empty and filled sample tubes was calculated from several weighings made for each condition. The average weight and standard deviation was determined for both empty and filled sample tubes, and for blanks. The weight of an organic added to a sample tube was determined by weight difference. The imprecision for an organic due to weighing (S_w) was estimated from the standard deviation of the average weights of the empty (s_1) and filled (s_2) sample tube and of the blank, using the expression:

$$S_w = [s_1^2 + s_2^2 + (s_1^2 + s_2^2)_{blank}]^{1/2} \quad (1)$$

The relative imprecision due to weighing is obtained by dividing S_w by the weight of the organic and multiplying by 100. In the present study, the relative uncertainty did not exceed 1.8%.

The capillary tube sealing process results in a small, but real weight loss due to slight vaporization of the capillary material. During the time period in which samples in this study were prepared, blank tubes showed a weight loss ranging from 0.0003 to 0.0020 mg. The average weight loss due to sealing was 0.0013 ± 0.0008 mg. Depending on the weight of the organic (nominally, 0.05 to 0.5 mg) this represents a range from 0.4 to 1% relative uncertainty (one standard deviation) in the weight of the organic.

The uncertainties of the electrical scale (at 1 mg) and of the calibration weights (for a 10 mg weight) of the microbalance were specified to be ±0.05% and ±0.01%, respectively. The uncertainty of the microbalance was, hence, estimated to be $[(0.05)^2 + (0.01)^2]^{1/2}$, or 0.05%, relative. The top-loading balance used to weigh the cylinder and matrix gas was calibrated with NBS weights and determined to be accurate to within ±0.1g. For the mixtures prepared, the weight of the matrix gas ranged from 800g to 4200g, resulting in an estimated uncertainty of less than 0.05% relative.

The estimated uncertainty of the preparation procedure ($s_{prep,est.}$) due to the above error estimates was then calculated from the general expression:

$$s_{prep,est.} = [a^2 + b^2 + \ldots + n^2]^{1/2} \quad (2)$$

Typical estimated uncertainties for the preparation procedure ranged from 0.4 - 1.0%.

Precision of Gravimetric Preparation

The six gravimetrically prepared mixtures were analyzed relative to each other using a GC-FID system. Several injections were made on each sample, with one being used as a control (sampled first and last) to adjust for instrumental drift. All averaged responses for each organic were then normalized to the control. A linear regression of area response vs. gravimetric concentration was prepared, with the analyzed concentrations determined from the regression. Table I compares the gravimetric and analyzed concentrations for each organic in each of the six standards. The mean preparatory imprecision of a given organic determined in this intercomparison across all cylinders (calculated from the difference between the predicted gravimetric and the analyzed concentrations) ranged from 0.5 to 3.6%, relative (Table I). Hence, the precision of the gravimetric method (s_{prep}) is demonstrated by the differences in intercomparing predicted and analyzed concentrations.

Precision of Analysis

Table II shows the FID response of the organics to replicate injections of 10 cm^3 samples taken from one of the six cylinders (cylinder no. AAL-12029). The imprecision for repeated analysis of the organics ranged from 0.4% to 4.7%, reflecting the precision of mean concentrations determined by analysis (s_{anal}).

Conclusions

The total uncertainty (95% confidence limit) of the gravimetric concentrations of the mixtures is calculated from the expression $2[s^2_{prep} + s^2_{anal}]^{1/2}$, where s_{prep} and s_{anal} represent one standard deviation of the imprecisions in the preparatory and analysis steps, respectively, determined analytically (Tables I and II, respectively). Typical imprecisions in the preparation procedure and in the analysis, and the resultant total uncertainties of the gravimetric concentrations of the organics are shown (for cylinder no. AAL-12029) in Table III. The relatively low imprecisions for the preparation step of mixtures in the 10-40 ppb range was considered excellent, considering that the limiting factors are the reliability in weighing volatile organics at levels of less than 0.5 mg and the reliability in their quantitative transfer to an evacuated cylinder. The total uncertainties of the gravimetric concentrations of benzene and vinyl chloride were less than those for the highly halogenated species, chloroform, carbon tetrachloride, and tetrachloroethylene. This can be attributed to the low signal and associated higher analytical imprecision using an FID (see Table II) for the halogenated organics. An ECD currently is being employed for the analysis of other halogenated organic mixtures at these concentration levels. Preliminary results indicate that an improvement in precision due to enhanced detection response of at least one order of magnitude is attainable. This should substantially decrease the total uncertainty of the concentrations of the organics in these and future ultratrace organic standards.

Summary

The study described in this paper is intended to illustrate our capabilities for gravimetrically preparing accurate concentrations of multicomponent toxic organic mixtures in the low ppb range and the procedures used for determining uncertainties of the gravimetrically prepared

concentrations of such mixtures. Numerous gravimetrically-based, trace organic mixtures have been prepared at NBS in this program over the past five years.

In earlier work, several mixtures of benzene in nitrogen were prepared in the 0.2 to 5 ppm range. When these mixtures were analyzed and compared against each other the differences between gravimetric and analyzed concentrations were found to be less than ±1% relative. As a crosscheck, gravimetrically-certified benzene permeation tubes (SRM 1911) were analyzed by sampling a gas stream containing the permeation tube at a known flow rate. A calibration curve was constructed from the responses of various sample sizes taken from the permeation tube system. Gravimetric cylinder standards of benzene were analyzed to be within 1.5% of their calculated concentrations, based on the permeation tube calibration curve. This demonstrated the feasibility of preparing gas cylinders containing organic mixtures using the microgravimetric technique. Subsequent analyses of these mixtures have revealed a high degree of concentration stability over several years.

A network of gravimetric trace organic standards have been prepared, contributing to the development of a systematic network of stable primary standards of volatile, toxic organics. This network currently covers about 15 different high-priority organics over the concentration range of 10 ppm to 1 ppb, and currently serves to provide the basis for data quality assurance and traceability of national monitoring efforts of toxic organics in the ambient air environment.

Table I. Comparison of Gravimetric and Analyzed Concentrations

Component	Cylinder	Gravimetric Conc. ppb	Analyzed Conc. ppb	Percent Difference[c]
Benzene	AAL-11133	99.9	99.9	0
	CAL-7493	46.8	46.7	-0.2
	CAL-8746	38.2	39.0	+2.1
	AAL-12029	37.0	36.3	-1.9
	AAL-7001	15.1	--[a]	--
	AAL-7009	7.60	7.56	-0.5
				$\bar{x}$ = 0.9
Vinyl Chloride	AAL-11133	152	152	0
	CAL-7493	86.0	85.1	-1.0
	CAL-8746	--[b]	23.0	--
	AAL-12029	24.5	24.8	+1.2
	AAL-7001	20.6	20.7	+0.5
	AAL-7009	5.54	5.54	0
				$\bar{x}$ = 0.5
Chloroform	AAL-11133	101	101	0
	CAL-8746	27.3	28.2	+3.3
	AAL-7001	19.9	19.9	0
	CAL-7493	19.8	20.5	+3.5
	AAL-12029	16.1	15.8	-1.9
	AAL-7009	4.68	4.59	-1.9
				$\bar{x}$ = 1.8
Carbon Tetrachloride	AAL-11133	107	107	0
	CAL-7493	35.1	32.5	-7.4
	CAL-8746	25.9	--[a]	--
	AAL-12029	23.5	23.6	+0.4
	AAL-7001	16.2	--[a]	--
	AAL-7009	6.76	6.68	-1.2
				$\bar{x}$ = 2.2
Tetrachloro-ethylene	AAL-11133	132	132	0
	CAL-7493	27.6	27.7	+0.4
	AAL-12029	13.6	13.7	+0.7
	AAL-7001	13.3	12.2	-8.3
	CAL-8746	10.3	11.2	+8.7
	AAL-7009	3.71	3.57	-3.8
				$\bar{x}$ = 3.6

[a] Particular organic showed interference by a trace impurity in the chromatogram.

[b] Analysis gave a reliable, consistent value which was different than the gravimetric value.

[c] Percent difference calculated from: [Analyzed conc.-Gravimetric conc.] x 100, divided by Gravimetric conc.; the mean percent differences ($\bar{x}$) represent the imprecision of the preparation method for each of the organics (s_{prep}).

Table II. Representative FID Response With 10-cm^3 Sampler to Consecutive Injections at Maximum Sensitivity (Cylinder AAL-12029)

	Benzene 37.0 ppb	Vinyl Chloride 24.5 ppb	Chloroform 16.1 ppb	Carbon Tetrachloride 23.5 ppb	Tetrachloro-ethylene 13.6 ppb
	896	221	50.6	66.6	144
	892	224	50.0	60.5	141
	888	224	46.5	64.7	134
	898	223	46.4	61.7	131
	894	223	51.1	62.3	146
AV	894	223	48.9	63.2	139
S	4	2	2.3	2.5	6
RSD[a]	0.4%	0.7%	4.7%	3.9%	4.6%

[a] These percent values represent the analytical imprecision for each of the organics (s_{anal}).

Table III. Typical Uncertainties in the Preparation and Analysis of Mixtures

Cylinder AAL-12029

Compound	Gravimetric Concentration	(s_{prep}) Preparatory Imprecision[a]	(s_{anal}) Analytical Imprecision[a]	Total Uncertainty[a,b]
Benzene	37.0 ppb	0.9%	0.4%	2.0%
Vinyl Chloride	24.5 ppb	0.5%	0.7%	1.7%
Chloroform	16.1 ppb	1.8%	4.7%	10.1%
Carbon Tetrachloride	23.5 ppb	2.2%	3.9%	9.0%
Tetrachloro-ethylene	13.6 ppb	3.6%	4.6%	11.7%

[a] Uncertainties are percent relative, representing 1 standard deviation.
[b] Total uncertainties (95% confidence) were calculated from the relationship, $2[(s_{prep})^2 + (s_{anal})^2]^{1/2}$.